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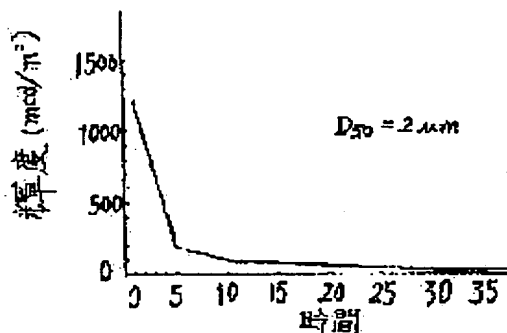
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## (54) LUMINOUS FLUORESCENT PARTICULATE POWDER AND ITS PRODUCTION

## (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a fine powdery luminous fluorescent body comprising fine particles having a strong emission intensity and a long emission time and excellent in water resistance.

SOLUTION: This luminous fluorescent body comprises aluminate salts of alkaline earth metals containing Eu as a main activator and has a composition expressed by the formula  $(A1-z-yDxEy)O.a(G1-zHz)2O3$  [A is one or more species of elements selected from a group comprising Mg, Ca, Sr and Ba of the alkaline earth metals and divalent metal Zn, D is Eu, an activator, E is one or more of elements selected from a group of the lanthanoid comprising Dy, Nd, Ho, Er, Tm, Yb, Lu and transition metals comprising Mn, Zr, Nb, Ti, Sb, Li, Ge, In and W, G is Al of the mother crystal body, H is B or Ga in the mother crystal body, (x), (y), (z) and (a) are each a number within the range expressed by  $0.0001 < x < 0.5$ ,  $0.0001 < y < 0.3$ ,  $0.0001 < z < 0.5$  and  $1.5 < a < 3.0$ .



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CLAIMS

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[Claim(s)]

[Claim 1] In the phosphorescent materials which consist of an aluminate of the alkaline earth metal which uses Eu as the main activator general formula  $(A_{1-z-y}D_xE_y)O_a(G_{1-z}H_z)2O_3$  (the inside A of a formula -- Mg of alkaline earth metal --) They are one sort or two sorts or more of elements chosen from the group which consists of calcium, Sr, Ba, and a divalent metal Zn, Dy of the lanthanoids whose D is Activator Eu and whose E is a coactivator, Nd, It is one sort or two sorts or more of elements chosen from the group which consists of Mn, Zr, Nb, Ti, Sb, Li, germanium, In, and W of Ho, Er, Tm, Yb, Lu, and transition metals, G is aluminum of a mother crystalline, and H is B of a mother crystalline, or Ga. Moreover, x, and y, z and a are the number of the range of  $0.0001 < x < 0.50.0001 < y < 0.30.0001 < z < 0.51.5 < a < 3.0$ , respectively.

Phosphorescent-materials particle powder characterized by having the presentation expressed.

[Claim 2] Phosphorescent-materials particle powder according to claim 2 with which particle powder with a particle size of 2micro or less occupies [ this particle powder ] 50 % of the weight or more.

[Claim 3]  $SrCl_2$  and  $6H_2O$  are used as a start raw material of Sr component, using  $AlCl_3$  and  $6H_2O$  as a start raw material of aluminum component.  $BaCl_2$  and  $2H_2O$  are used as a start raw material of Ba component.  $Eu_2O_3$ ,  $Dy_2O_3$  and  $H_3BO_3$  It uses as a start raw material of Eu, Dy, and B component, respectively. The manufacture approach of phosphorescent-materials particle powder of mixing the water solution of the above-mentioned chloride, and the water solution containing ammonium ion, making it reacting at 80 degrees C, cooling, calcinating the particle powder which filtered precipitation and was dried at an elevated temperature in a reducing atmosphere, and manufacturing phosphorescent-materials particle powder according to claim 1.

[Claim 4] The manufacture approach of the phosphorescent-materials particle powder according to claim 3 which calcinates the this dry particle powder under existence of carbon, such as activated carbon, and is performed in the reducing atmosphere of the carbon monoxide generated in air.

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[Translation done.]

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to phosphorescent-materials particle powder and its manufacture approach.

[0002]

[Description of the Prior Art] Phosphorescent materials are the ingredients which can conserve the light energy, can emit light over a long time in a dark place, and can be used for the various purposes, when daylight or the light from other light sources is irradiated. Most consisted of a sulfur compound, for example, as for the conventional phosphorescent materials, ZnS:Cu-Co or CaS:Co was used, as for these phosphorescent-materials powder, \*\*\*\*\* and since [ although light can be emitted, ] the luminescence time amount was about at most 1 ~ 2 hours, was deficient in chemical stability, and was inferior to a water resisting property and it was easy to deteriorate, under the ill condition, luminescence capacity declined rapidly and the fault that a use life was short had it in several 10 hours.

[0003] Moreover, although what added the radioactive substance to the phosphorescent-materials powder of the diameter of a sulfur compound can carry out long duration self-luminescence, also internationally, the disable of the use of the radioactive substance is carried out because of the radiation injury to the body, and environmental pollution.

[0004] The phosphorescent-materials powder which uses the aluminate of alkaline earth metal as a principal component in early the 1990s is proposed. Using Eu as an alkaline earth metal, the phosphorescent materials which activated the ulmin acid by this have high luminescence reinforcement, and its luminescence time amount is also as long as 24 hours or more, they are chemically stable, excellent in lightfastness, have the advantages, like a use life is also long, and are used broadly. For example, it is applied to fluorescence ink, fluorescent paint, fluorescence plastics, fluorescent glass, a fluorescence cloth, an ornament product, the low-strength light source, etc.

[0005]

[Problem(s) to be Solved by the Invention] The phosphorescent-materials powder which consists of an aluminate of the above-mentioned alkaline earth metal is alpha-aluminum 2O3. It is the solid-state powder of a very high degree of hardness of the shape of ceramics which mixes some kinds of required raw material compounds, is made to react at an elevated temperature 1300 degrees C or more, and is acquired. If it is very stable chemically and is not sufficiently high temperature, alkaline earth metal will not react, but the aluminate of a monoclinic system form will be refined for the first time at a hot reaction, and alpha-aluminum 2O3 is Eu 2O3. The activator which consists of a lanthanoids metallic element [ like ] is introduced during a crystal, and forms an emission center and a lattice defect. If this product of a high degree of hardness does not perform powerful grinding processing, it cannot be used as powder with a magnitude of several 10micro.

[0006] However, an energy of activation is absorbed by the defect of the crystal produced at the time of grinding, and luminescence declines. If particle size is set to 10micro or less, the reinforcement of luminescence will fall rapidly, and if particle size is set to 3micro or less,

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temperature in a reducing atmosphere, and manufacturing phosphorescent-materials particle powder according to claim 1 be a summary.

[0013]

[Embodiment of the Invention] Next, although an example explains concretely the gestalt of operation of the phosphorescent-materials particle powder of this invention, and its manufacture approach, this invention is not limited to this example.

[0014] [Example]

SrCl2 and 6H2 O 260gAlCl3 and 6H2 O 683.2gBaCl2 and 2H2 O The water solution which dissolved 1.74 g in 5000ml of ion exchange water is used as Solution A, and it is 2 (NH4) CO3. Let the water solution which dissolved 488g in 2000ml of ion exchange water be Solution B. It cools and precipitation is filtered, after mixing Solution A and Solution B in 5000ml of 80-degree C ion exchange water and maintaining for 15 minutes at 80 degrees C. After drying and grinding the precipitation, it put into the crucible, and at 1300 degrees C, it calcinated for 1 hour and cooled. To this, Eu 2O3 1.98gD(ies) 2O3 2.8gSb(s) 2O3 30.7gH(s)3 BO3 28g oxalic acid (two matters of chance) 1.4 After mixing g and carrying out wet grinding with a ball mill for 4 hours, it put into the end crater which gets 750ml, 3-5cm space was left to the upper limb of a crucible, the end crater into which two granularity activated carbon was put and which gets 30ml was placed, and the end crater which gets 750ml was sealed with the lid. It calcinated at 1300 degrees C at the electrical machinery furnace for 2 hours. The above-mentioned activated carbon reacts with the oxygen in air, a carbon monoxide is generated, and baking is performed in the reducing atmosphere of a carbon monoxide. The product was cooled to 400 degrees C, and it took out from the electrical machinery furnace, and ground again after cooling to the room temperature, screen analysis was carried out with the screen of 350 meshes, and the weight of a particle-size part 2micro or less obtained 50% (50= 10micro of D) of particle powder. The obtained particle powder had strong luminescence reinforcement, and luminescence time amount was long and was waterproof good phosphorescent-materials particle powder. The particle size distribution of particle powder are shown in drawing 2, and the temporal response of luminescence reinforcement is shown for the emission spectrum in drawing 1 at drawing 3, respectively. The phosphorescent-materials particle powder of this invention has very little dispersion in particle size distribution, and is particle powder of sharp particle size distribution.

[Drawing 1]

[Drawing 2]

[Drawing 3]

[0015] [Example of a comparison] In the example of this invention SrCl2 and 6H2 O, AlCl3 and 6H2 O. Instead of BaCl2 and 2H2 O, they are SrCO3, alpha-aluminum 2O3, and BaCO3, respectively. These are mixed using the amount equivalent to the number of mols of the element used in the example 1. Having used for this in the example Eu 2O3 of tales doses, Dy 2O3, and Sb 2O3, H3 BO3 And oxalic acid (two matters of chance) was added, it put into the ball mill, and mixed and ground for 3 hours, like the example, at 1300 degrees C, it calcinated for 2 hours, and screen analysis was ground and carried out, and the weight of a particle-size part 10micro or less obtained 50% (50= 10micro of D) of powder, and measured the luminescence property. The result is shown in drawing 4.

[Drawing 4]

[0016] If drawing 3 is compared with drawing 4, the particle powder of 50= 2micro of D of the phosphorescent materials obtained by the manufacture approach of this invention is excellent in both luminescence reinforcement and luminescence time amount as compared with the powder with a comparatively big particle size of 50= 10micro of D of the phosphorescent materials obtained in the example of a comparison of a conventional method more than equivalent.

[0017]

[Effect of the Invention] According to the manufacture approach of the phosphorescent-materials particle powder of this invention, phosphorescent-materials particle powder with a very small particle size can be obtained. Even if the phosphorescent-materials particle powder of this invention is particle powder of 50= 2micro of D, luminescence reinforcement is strong, luminescence time amount is long, it excels in a water resisting property, and the

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luminescence will become feeble, and it becomes difficult to present practical use. In order to have used phosphorescent-materials powder for applications, such as fluorescence ink for offset printing, a fluorescence toner for electronic copying machines, and a color for fiber dyeing, the powder of a particle was very required and it was impossible to have obtained the particle powder which has luminescence reinforcement sufficient with the phosphorescent-materials powder which consists of an aluminate of the conventional well-known alkaline earth metal. [0007] On the other hand, in case +2 and + trivalent ion work as activators of a fluorescent material in aluminate phosphorescent materials, luminescence of a completely different spectrum is carried out. In the aluminate of alkaline earth metal, only divalent Eu ion can form a lattice defect. In case phosphorescent materials are manufactured, it is usually + trivalent Eu 2O3. Although it considers as Eu ion source, and it adds and mixes and being heated to an elevated temperature, it is necessary to return + trivalent Eu during a pyrogenetic reaction at + divalent Eu. Therefore, it is necessary to perform this solid phase reaction in a reducing atmosphere, and the reduction yield to + divalent Eu of + trivalent Eu determines the quality of phosphorescent materials. Although the conventional approach reacted in the nitrogen gas stream which contains hydrogen gas about 5% and Eu ion was returned, the reaction needed to be performed in the well-closed container, actuation became complicated, the production cost increased, and mass production method was difficult again.

[0008] Therefore, luminescence reinforcement of this invention is high and luminescence time amount aims at offering the long phosphorescent materials of the shape of very small impalpable powder of a particle excellent in the water resisting property.

[0009] Furthermore, other purposes of this invention aim at offering the approach of manufacturing the phosphorescent-materials particle powder which excelled [ approach / very easy ] in quality.

[0010]

[Means for Solving the Problem] As a result of repeating research wholeheartedly, this invention person that the above-mentioned purpose should be attained An aluminum chloride, Chlorides, such as a strontium chloride and barium chloride, respectively Aluminum. It uses as a start raw material of components, such as strontium and barium. Eu 2O3, Dy 2O3 and H3 BO3 It uses as a start raw material of Eu, Dy, and B component, respectively. By drying the precipitation which mixed some water solutions of these components with the water solution containing ammonium ion, and was obtained, and carrying out heating baking of the particle powder of the acquired predetermined presentation It came to complete a header and this invention for the phosphorescent materials of the shape of very small particle powder of a particle which whose luminescence reinforcement was high and were excellent in the water resisting property with long luminescence time amount being obtained.

[0011] Namely, this invention is set to the phosphorescent materials which consist of an aluminate of the alkaline earth metal which uses Eu as the main activator. general formula (A1-z-y D<sub>x</sub> E<sub>y</sub>) O-a (G1-z H<sub>z</sub>) 2O3 (the inside A of a formula — Mg of alkaline earth metal —) They are one sort or two sorts or more of elements chosen from the group which consists of calcium, Sr, Ba, and a divalent metal Zn. Dy of the lanthanoids whose D is Activator Eu and whose E is a coactivator, Nd. It is one sort or two sorts or more of elements chosen from the group which consists of Mn, Zr, Nb, Ti, Sb, Li, germanium, In, and W of Ho, Er, Tm, Yb, Lu, and transition metals, G is aluminum of a mother crystalline, and H is B of a mother crystalline, or Ga.

Moreover, x, z and y, z and a are the number of the range of 0.0001< x<0.50.0001<y<0.30.0001<z<0.51.5<a<3.0, respectively. Let the phosphorescent-materials particle powder characterized by having the presentation expressed be a summary.

[0012] AlCl3 and 6H2 O are used for other this inventions as a start raw material of aluminum component. BaCl2 and 2H2 O are used as a start raw material of Ba component, using SrCl2 and 6H2 O as a start raw material of Sr component. Eu 2O3, Dy 2O3, and H3 BO3, respectively Eu, Use as a start raw material of Dy and B component, mix the water solution of the above-mentioned chloride, and the water solution containing ammonium ion, and it is made to react at 80 degrees C. Let the manufacture approach of phosphorescent-materials particle powder of cooling, calcinating the particle powder which filtered precipitation and was dried at an elevated

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phosphorescent materials of the shape of very small particle powder of the particle can be used also for the application of fluorescence coloring agents, such as the fluorescence ink for printing, such as offset printing and ink jet printing, a fluorescence toner for electronic copying machines, fluorescent dye for fiber dyeing, a synthetic-resin pellet, a synthetic-resin film, and a coating, etc.

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